



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁴ : B32B 9/04, 17/04, 19/02	A1	(11) International Publication Number: WO 86/ 05445 (43) International Publication Date: 25 September 1986 (25.09.86)
<p>(21) International Application Number: PCT/US86/00553</p> <p>(22) International Filing Date: 14 March 1986 (14.03.86)</p> <p>(31) Priority Application Number: 8500810</p> <p>(32) Priority Date: 20 March 1985 (20.03.85)</p> <p>(33) Priority Country: NL</p> <p>(71) Applicant (for all designated States except US): THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US).</p> <p>(72) Inventor; and (75) Inventor/Applicant (for US only) : VAN, Dinh, Phan [BE/BE]; Spinmoleinplein 246, B-9000 Gent (BE).</p> <p>(74) Agent: MACLEOD, Roderick, B.; The Dow Chemical Company, P.O. Box 1967, Midland, MI 48641-1967 (US).</p>		<p>(81) Designated States: AU, BE (European patent), BR, DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, NL (European patent), SE (European patent), US.</p> <p>Published <i>With international search report.</i> <i>With amended claims.</i></p>
<p>(54) Title: REINFORCED, PLASTIC POLYMER, COMPOSITES AND A METHOD FOR PREPARING SAME</p> <p>(57) Abstract</p> <p>Reinforced composites comprise a plastic polymer matrix having a reinforcing agent dispersed throughout the polymer matrix wherein the reinforcing agent is coated with an interlayer consisting of a rubber which is compatible with the plastic polymer or is made compatible with the plastic polymer and which is adhered, through chemical bonding, to the reinforcing agent. The elastomeric interlayer serves as a compatibilizing layer between the plastic polymer matrix and the reinforcing agent such that both the reinforcing agent and plastic polymer matrix positively contribute to the properties of the resulting composite and such that the reinforced composites exhibit an unexpectedly superior balance of physical properties to the reinforced, plastic polymer, composite. Moreover, the physical integrity of the reinforcing agent coated with the elastomer is significantly improved.</p>		

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REINFORCED, PLASTIC POLYMER, COMPOSITES
AND A METHOD FOR PREPARING SAME

The present invention relates to reinforced, plastic polymer, composites and to a method for preparing a polymer reinforced with a reinforcing agent grafted with an elastomer. It also relates to the
5 intermediate product of a reinforcing agent grafted with an elastomer.

To change the properties of plastic materials, (as defined hereinafter) it has become a common practice to incorporate one or more adjuncts such as fillers,
10 lubricants, hardeners, stabilizers or reinforcing agents within the plastic material. For example, incorporating a mineral fiber such as chopped glass fibers into the plastic polymer material will often result in improved high temperature and tensile properties,
15 increased rigidity and decreased shrinkage. However, the glass fiber functions, in other respects, more or less as a filler than as a reinforcing agent. Specifically, any enhancement in some physical properties of the plastic material due to the incorporation of the



glass fibers in the plastic polymer is accompanied by a coincident and significant reduction in other physical properties such as impact strength and toughness.

The glass strands or glass fibers employed
5 in preparing conventional reinforced composites are typically made up of a plurality, e.g., from 200 to 1500, monofilaments or microfibers. The surface of each filament as well as the surface of the resulting strand or fiber is generally coated with a
10 coupling agent and/or sizing agent which keeps the filaments together and maintains the integrity of the strand or fiber. It is the strand or fiber which is generally blended with the polymer to prepare the reinforced composite.

15 A significant amount of work has been conducted regarding composites containing glass and a plastic polymer. See, specifically, "Composite Interfaces, Myths, Mechanisms and Modifications" by John L. Kardos published in Chemtech,
20 July 1984, pages 430-434 and the articles "Bonding Rigid Polymers to Mineral Surfaces Through a Rubbery Interface", by E. P. Plueddermann, presented at the 29th Annual Technical Conference of the Reinforced Plastics/Composites Institute of the Society of Plastics
25 Industry, Inc., 1975; "Additives - Their Effect on Parameters and Production Performance" by R. E. Lavengood and M. J. Michno Jr., Process Division Technical Conference, Engineering Properties Structure Division of the Society of Plastic Engineers in 1975, pages
30 126-145 and "Adhesion to Silane-Treated Surfaces Through Interpenetrating Networks: by E. P. Pluedderman

and G. L. Stark, 35th Annual Conference, Reinforced
Plastics Composites Institute, Society of the Plastics
Industry (SPI), 1980.

In one of the described methods, it is pro-
5 posed to deposit a flexible inner layer of a liner
polyamide modified epichlorohydrin/bisphenol A type
epoxy resin on the fiber in preparing a reinforced
composite of a brittle epoxy resin reinforced with
short glass fiber. However, this and the other
10 described composites do not possess the desired
impact strengths or balance of physical properties
required for commercial application.

An alternative method proposed by these
articles for preparing a composite of a glass rein-
15 forcing agent and a plastic polymer matrix involves
coating the glass with a silane coupling or wetting
agent. A suitable coupling agent is a silane con-
taining a reactive group which is capable of reacting
with the plastic polymer matrix. For example, in
20 preparing a reinforced composite from a styrenic
polymer resin and glass fibers, it has been sug-
gested to coat the glass fibers with a coupling
agent containing ethylenic unsaturation, e.g., a
vinyl silane. When glass fibers, coated with a
25 vinyl silane coupling agent, are melt blended, at
sufficiently high temperatures, with a styrenic
polymer resin, the ethylenic unsaturation of the
vinyl silane (or, more specifically, the free radicals
formed from this unsaturation) may react with some
30 limited amount of the styrenic polymer resin, thereby
bonding the styrenic polymer to the glass fiber.

Although the properties of the resulting reinforced composite are somewhat improved as compared to a composite prepared using glass fibers which have not been coated with a silane coupling agent, the toughness or impact strengths of the composites continue to remain even lower than that of the original plastic polymer material. Moreover, due to handling problems (particularly the problems associated with feeding the glass to a melt blending unit without so-called "hay-stacking") the processing of the glass fibers to achieve a uniform dispersion of the glass throughout the polymer matrix is difficult. The resulting non-uniform dispersion of the glass throughout the polymer creates less desirable physical properties to the resulting reinforced composite.

To improve the handling characteristics of the glass and thereby improve the dispersion of glass fibers throughout the polymer matrix of the final composite, it has been proposed to prepare a glass reinforced composite by preparing a glass concentrate capsule of a plurality of glass strands comprising a plurality of microfibers and a thermoplastic resin matrix such as a poly(vinyl chloride) or polystyrene and subsequently blending the glass concentrate capsule in a thermoplastic resin. See, specifically, U.S. Patent No. 3,671,378. In the described glass concentrate capsule, the individual microfilaments in the glass strands, the glass strands themselves and the encapsulated bundle of glass strands are encapsulated within the thermoplastic resin matrix. When blended with the thermoplastic resin, the glass fibers in the glass concentrate capsule become relatively uniformly

dispersed throughout the polymer matrix. Due to increased uniformity of the dispersion of the glass fibers throughout the polymer matrix, the properties of the resulting glass reinforced composite approach are also improved and approach the properties which would be expected of a composite prepared from an ideally wetted glass fiber. Unfortunately, again, these improved physical properties do not include significant increases in the impact and toughness properties of the resulting composites.

It has also been proposed to prepare a particulate of filamentary mineral reinforced thermoplastic polymer composition by coating the mineral with a thin polymer interactive layer, at a thickness of from 5 to 500 Angstroms, of silicon-free and heavy metal free, organic molecules chemically bonded to the mineral's surface by covalent bonding. (See, U.S. Patents No. 4,405,727). As in similar composites, the coating on the mineral promotes the adhesion to or compatibility of the mineral with the plastic polymer matrix. Although the impact strengths of the composite are marginally increased, in some cases, upon the addition of small amounts of the mineral reinforcing agent to the plastic polymer matrix, in general, the impact strengths decrease with increasing amounts of the mineral composite.

A glass fiber, reinforced thermoplastic resin has also been prepared by coating glass fibers, which can be coated with a sizing or coupling agent, with a functional copolymer of at least one mono-

vinylidene aromatic compound, e.g., styrene, and a functional monomer, e.g., N-isobutoxymethylacrylamide and subsequently dispersing the thus coated glass fibers in the polymer forming the matrix phase. (See, specifically, European Patent Application, Publication No. 0 081 230.) The resulting composition (which comprises a rigid thermoplastic resin, reinforcing glass fibers and the functional monomer) is shown to possess improved impact and high temperature properties when compared to the thermoplastic resin material alone. Although the described glass reinforced composites generally exhibit better high temperature properties and, to a lesser extent, impact properties, than the same polymer reinforced with untreated glass fibers, reinforced composites of yet higher impact strengths and an improved balance of physical properties are desired.

In contrast to the aforementioned prior art one aspect of the present invention is a composite of the type having a plastic polymer matrix and having a reinforcing agent dispersed throughout the polymer matrix and characterized in that the reinforcing agent is coated with an interlayer consisting of a rubber which (1)(a) is compatible with the plastic polymer or (b) is made compatible with the plastic polymer and (2) is adhered, through chemical bonding, to the reinforcing agent.

In a second aspect of the invention, there is a reinforced polymer composite of the type including (a) a plastic polymer matrix; (b) a reinforcing agent; and (c) an interlayer between the polymer and the

reinforcing agent; characterized in that the interlayer (1) is elastomeric; and (2) is directly or indirectly bonded to the reinforcing agent.

In contrast to the mineral reinforced composites of the prior art, the plastic polymer matrix and the modified reinforcing agent of this invention interact through the interlayers such that both the reinforcing agent and plastic polymer matrix positively contribute to the properties of the resulting composite. Although adhesion or compatibility between the plastic polymer matrix and the reinforcing agent is required, in and of itself, it is not sufficient to create this interaction and cooperation. The elastomeric interlayer in this invention provides not only the necessary adhesion/compatibility as well as providing for the desired interaction and cooperation between the two phases during both (1) the compounding stage to form the composite, and (2) after formation of the composite. This interaction and cooperation of the reinforcing agent and the plastic polymer matrix imparts an unexpectedly superior balance of physical properties to the reinforced, plastic polymer, composite. Specifically, the reinforced, plastic polymer composites of the present invention exhibited an exceptional balance of toughness, tensile strength and high temperature properties when compared to the pure plastic polymer material containing no reinforcing agent or to a plastic polymer material reinforced with an untreated reinforcing agent according to the methods employed heretofore.

Moreover, the physical integrity of the reinforcing agent coated with the elastomer is significantly improved. Specifically, the integrity of

the reinforcing agent can be sufficiently maintained during normal, subsequent melt processing. More particularly, the reinforcing agent maintains a great degree of integrity than glass fiber which has not
5 been so grafted and coated and which is subjected to the same process operations. For example, breakage of the glass fibers during compounding can be reduced.

In another aspect, the present invention is a method for preparing the reinforced plastic polymer
10 composite. The method comprises the initial step of grafting the mineral reinforcing agent with a layer of the elastomeric material and thereafter dispersing the elastomeric coated, reinforcing agent throughout the plastic polymer matrix.

15 In a preferred embodiment, the elastomer is chemically bonded to the reinforcing agent using a coupling agent having functional groups reactive with the reinforcing agent and the elastomeric material. In this manner, the coupling agent is employed to chem-
20 ically bond the elastomer to the reinforcing agent.

Due to their outstanding combination of toughness, tensile strength and high temperature properties, the reinforced, plastic polymer composites of the present invention are useful in a wide variety
25 of applications such as automotive products; molded casings for household goods and appliances and other engineering applications; structural applications such as for building and construction purposes; and plastic pipes.

The term "plastic" is used conventionally herein and refers to a polymer which can be formed or molded under heat and pressure in its raw (i.e., "unworked" or virgin) state and is capable of being

5 machined in its hardened state. The plastic material can be of the thermoplastic type (i.e., those which can be resoftened to their original condition by heat), or thermosettable (i.e., those which when heated solidify or set irreversibly and cannot subsequently be resoft-

10 ened to their original conditions by heat).

Plastic materials are well known to those skilled in the art and reference is made thereto for the purposes of this invention. Representative thermosettable plastic materials include vinyl ester resins,

15 epoxy resins, some polyester resins, amino resins, silicones and phenolic resins. Representative thermoplastic materials include polymeric resins derived from one or more monovinylidene aromatic compounds such as styrene and, optionally, one or more monomers copolymer-

20 izable therewith such as an ethylenically unsaturated nitrile, including rubber-reinforced polymers of this type commonly referred to as high impact polystyrene ("HIPS") and ABS type resins; so-called "acrylic resins" such as poly(methylmethacrylate); polyolefins, including

25 high density, low density and linear low density polyethylenes, and polypropylene; nylons; polycarbonate; polyphenylene oxides and poly(ether ethyl ketone). Polyurethanes and isocyanurate modified polyurethanes of the thermosettable or thermoplastic type can also be

30 employed as the plastic material. Some polyesters are thermoplastic. Mixtures of two or more plastic materials can also be employed. In general, the composites of the present invention are preferably prepared from one or more thermoplastic materials.

Thermoplastic materials found to be of particular interest in the practice of the present invention are polymer resins prepared from one or more monovinylidene aromatic compound and, optionally, one or more monomers copolymerizable therewith (hereinafter referred to as styrenic polymer resins); polycarbonates, polyphenylene oxides and polyolefins, particularly polyethylenes.

Representative monovinylidene aromatic compounds useful in preparing the styrenic polymer resins include styrene; alkyl-substituted styrenes such as alpha-alkylstyrenes (e.g., alpha-methylstyrene and alpha-ethylstyrene); ring-substituted styrenes (e.g., vinyl toluene, particularly p-vinyltoluene, o-ethylstyrene and 2,4-dimethylstyrene); ring-substituted halo styrenes such as chlorostyrene and 2,4-dichlorostyrene; and styrenes substituted with both a halo group and an alkyl group such as 2-chloro-4-methylstyrene and vinylanthracene. Copolymers of two or more monovinylidene aromatic compounds can also be employed. In general, the preferred monovinylidene aromatic compound employed in preparing the plastic polymer is (1) styrene, or (2) a combination of styrene and alpha-methylstyrene wherein from 10 to 50, preferably from 15 to 40, weight percent of the total weight of the styrene and alpha-methylstyrene is alpha-methylstyrene. Styrene is the most preferred monovinylidene aromatic compound.

Optionally, the monovinylidene aromatic compound can be copolymerized with one or more other comonomers to form the plastic polymer. Representative of such other comonomers include the unsaturated nitriles

such as acrylonitrile, ethacrylonitrile, methacrylonitrile and mixtures thereof; the α,β -ethylenically unsaturated carboxylic acids and esters thereof such as acrylic acid, methacrylate, methylmethacrylate, ethylacrylate and 2-ethylhexylacrylate; the acid anhydrides such as maleic anhydride; the ethylenically unsaturated amides such as acrylamide and methacrylamide; divinyl aromatic compounds such as divinyl benzene; vinylidene chloride and vinylidene bromide and vinyl esters such as vinyl acetate.

If prepared as a copolymer with one or more non-aromatic comonomers, the styrenic polymer resin is often conventionally prepared from at least one monovinylidene aromatic and at least one unsaturated nitrile. Preferred of the unsaturated nitriles is acrylonitrile. In general, the copolymer matrix will comprise from 5 to 35, preferably from 15 to 25, weight percent of the unsaturated nitrile and from 95 to 65, preferably from 85 to 75 weight percent of the monovinylidene aromatic, said weight percents being based on the total amount of monovinylidene aromatic and unsaturated nitrile.

If employed, any of the comonomers other than an unsaturated nitrile will generally be employed in amounts of less than 10, more generally less than 5, weight percent based on the total weight of the monomers employed in preparing the continuous polymer matrix phase of the mineral-reinforced styrenic polymer resin.

The olefinic polymers advantageously employed in the practice of the present invention are homo- or

copolymers of ethylene and include low density polyethylene, high density polyethylene, linear low density polyethylene and copolymers of ethylene with minor amounts of other comonomers such as vinyl acetate, styrene and/or alkyl acrylates. The terms "low density polyethylene"; "high density polyethylene" and "linear low density polyethylene" are well known in the art and used conventionally herein. The low density polyethylenes are generally homopolymers of ethylene exhibiting a density from 0.91 to 0.94 grams per cubic centimeter (g/cm³) at 20°C. Illustrative of such polymers and the techniques for their preparation are described in U.S. Patent Nos. 3,756,996 and 3,628,981. The high density polyethylenes are also generally homopolymers of ethylene but exhibit a density of at least 0.94 g/cc at 20°C, and particularly with a density of from 0.96 to 0.99 gram g/cc. Alternatively, linear low density polyethylenes are copolymers of ethylene with one or more alpha-olefins having three or more carbon atoms (such as a copolymer of ethylene with butene-1, octene-1 or hexene-1). Representative linear low density polyethylenes and methods for the preparation are disclosed by U.S. Patent Nos. 2,825,721; 2,993,876; 3,250,825 and 4,204,050.

Polycarbonates are the reaction product of a dihydric phenol and a carbonate diester or a carbonyl halide, preferably phosgene. They include the copolymers of the polycarbonates such as the polyester carbonates derived from a dihydric phenol, a carbonate diester or carbonyl halide and a diacid chloride. Representative dihydric phenols include the bis-(hydroxyphenyl)alkylidenes such as 2,2-bis-(4-hydroxyphenyl)propane (i.e., bisphenol A);

2,4-dihydroxyldiphenylmethane; bis-(2-hydroxyphenyl)-methane; 1,1-bis-(4-hydroxyphenyl)ethane and other bisphenol A type diols as described in U.S. Patent No. 3,028,365, as well as the corresponding aromatically substituted or aliphatically substituted dihydric phenols. Of the foregoing dihydric phenols, bisphenol A and substituted bisphenol A are preferred, with bisphenol A being most preferred.

In addition, rubber-reinforced polymer resins (i.e., a polymer resin having discrete particles of a rubber dispersed throughout the plastic polymer matrix phase) are also suitably employed herein.

It is preferred that the plastic polymers used in this invention have Viscat softening points greater than 25°C; and more preferably greater than 50°C; as measured by ASTM 1525 B.

Materials advantageously employed as the reinforcing agent in the practice of the present invention include steel, aramid, high strength polyethylene fibers (such as described in U.S. Patent Nos. 4,276,348 and 4,356,138), graphite, mica and glass. Other minerals such as titanium dioxide or potassium titanate can also, but less preferably, be employed. A highly preferred reinforcing agent is glass. The reinforcing agent can be employed in a variety of different shapes and sizes including powders, spherical beads, granules, monofilaments, fibers and fabrics depending on the particular end use application of the reinforced, plastic polymer composite and the properties desired for the desired end-use application.

Advantageously, the reinforcing agent is employed as a fiber or monofilament, with monofilaments being preferred. More preferably, the reinforcing agent is glass monofilament, particularly monofilaments having a diameter from 1 to 100, more advantageously from 5 to 50 micron. Most preferably, chopped glass monofilaments having, a length, in the composite, from 0.05 to 50, preferably from 0.1 to 20, most preferably from 0.5 to 10, millimeters and a diameter from 5 to 20, preferably from 8 to 15, micron. Non-alkaline fillers and reinforcing agents may be used in this invention, and often are preferred.

In the practice of the present invention, the reinforcing agent is grafted and coated with an elastomer. The term "elastomer" is used conventionally herein and refers to both natural rubbers and synthetic organic elastomeric materials (rubbers). In general, the rubber employed in preparing the elastomeric coating will be a homopolymer or a copolymer of an alkadiene, including functionally terminated alkadiene polymers. Preferably, the alkadiene is a 1,3-conjugated diene such as butadiene, isoprene, chloroprene, piperylene. Representative copolymers include copolymers of the 1,3-conjugated dienes with a monovinylidene aromatic compound such as styrene (which is generally chemically bonded in blocks or grafted branches to the alkadiene polymer); an α,β -ethylenically unsaturated nitrile such as acrylonitrile and/or an alkyl ester of an acrylic or methacrylic acid such as methyl methacrylate or an alpha-olefin such as ethylene or propylene. A rubber useful in the practice of the present invention, when prepared exclusively from an alkadiene or as a random

copolymer of an alkadiene and a comonomer, will exhibit a single second order transition temperature which is not higher than 0°C and preferably not higher than -20°C as determined using conventional techniques, e.g., ASTM Test Method D-746-52T. Alternatively, a copolymer having one or more polymer blocks grafted or bonded to a polymer block of an alkadiene will exhibit two or more glass transition temperatures. In the practice of the present invention, such block copolymer can be employed as a rubber provided a glass transition temperature of less than 0°C, preferably less than -20°C, can be assigned to the rubbery block of the copolymer. In this case, the block exhibiting such a glass transition temperature is considered to be the rubber and any other blocks not exhibiting such a glass transition temperature are not considered to be rubber. Silicon and acrylic rubbers as well as elastomeric polyurethanes can also be employed as the rubber herein. A copolymer of ethylene, propylene and, optionally, a non-conjugated diene can also be employed in preparing the elastomeric coating. These elastomeric materials also exhibit a glass transition temperature of less than 0°C, preferably less than -20°C.

The elastomers most advantageously employed in preparing the elastomeric coating are dependent on a variety of factors including the specific reinforcing agent and plastic polymer employed and the desired properties of the reinforced, plastic polymer, composite. Specifically, although not being bound by the theory, it is believed that the rubber of the elastomeric coating acts as an "interlayer" between the mineral reinforcing agent (which generally possess an extremely

high Young's modulus but relatively low elongation) and the polymer matrix (which generally possess a significantly lower Young's modulus but generally higher elongation). The rubber itself will generally possess
5 a significantly lower Young's modulus but a significantly higher elongation than both the reinforcing agent and the plastic polymer.

The elastomers most advantageously employed in preparing the elastomeric coating are dependent on a
10 variety of factors including the specific reinforcing agent and plastic polymer employed and the desired properties of the reinforced, plastic polymer, composite. Specifically, although not being bound by the theory, it is believed that the rubber of the elastomeric
15 coating acts as an "interlayer" between the mineral reinforcing agent, which generally possess an extremely high Young's modulus but relatively low elongation, and the polymer matrix which generally possess a significantly lower Young's modulus but generally higher
20 elongations. The rubber itself will generally possess a significantly lower Young's modulus but a significantly higher elongation than either the reinforcing agent or the plastic polymer.

To effectively provide the required interaction and cooperation between the reinforcing agent
25 and the plastic polymer matrix, the elastomer interlayer in the final composite is at least 500 Å but less than 50,000 Å. More preferably, the thickness of the elastomeric interlayer is from 1000 to 20,000 Å, most
30 preferably from 2500 Å to 10,000 Å. In the practice of this invention, it has been found that compounding of

the coated reinforcement and plastic polymer can result in redistribution of the elastomeric material within the polymer matrix.

To optimize the effects of the rubber as an interlayer, i.e., to optimize the physical properties of the reinforced, plastic polymer, composite, the elastomeric coating is compatible with the polymer matrix or the elastomeric coating is made compatible if not so compatible. By the term "compatible", it is meant that the elastomer and polymer matrix, although not necessarily in thermodynamic equilibrium, behave mechanically as if they were in thermodynamic equilibrium. This compatibility is conventionally evidenced by one or more of the following factors: (1) a negative Flory-Huggins interaction parameter such as measured using inverse gas chromatography, (2) a single glass phase transition temperature, (3) a volume increase on mixing (4) the absence of X-ray or neutron scattering characteristics of microphases greater than molecular size and (5) a change in the frequency or intensity in Infrared peaks or a broadening or shifting of differential scanning calorimeter traces.

There are a variety of different methods to achieve the desired compatibility. For example, the rubber employed in preparing the elastomeric coating can be reactive with the monomer(s) used in preparing the continuous matrix phase of the composite. As an example, a reinforced styrenic polymer composite of the present invention can be prepared by polymerizing the monovinylidene aromatic compound and, optionally, comonomer(s), in the presence of a reinforcing agent

coated with an elastomeric layer of an alkadiene polymer such as a 1,3-conjugated diene, e.g., polybutadiene. The ethylenic unsaturation of the alkadiene rubber provides reactive sites for chemical reaction (i.e., the grafting reaction) of the rubber to the monovinyli-
5 denic aromatic compound and/or other monomer(s) used in preparing the polymer matrix phase. This grafting reaction provides the necessary compatibility between the elastomeric coating and the matrix phase.
10 Preferred rubbery polymers for preparing the elastomeric coating in such case are the homopolymers of 1,3-butadiene. Since a polymerized monovinyli-
denic aromatic resin contains few, if any, residual ethylenic unsaturation, it is not generally sufficient to prepare
15 the reinforced, plastic polymer, composites from a reinforcing agent coated with a homopolymer of 1,3-conjugated diene and a previously prepared styrenic polymer.

Similarly, the rubber can possess groups
20 reactive with the polymer of the continuous matrix phase such that the rubber and the polymer are capable of reacting upon dispersing the elastomeric reinforcing agent throughout the polymer matrix phase. For example, a carboxy terminated rubber such as a carboxy terminated
25 polybutadiene rubber ("CTB" rubber) is capable of reacting with an epoxy resin. Therefore, a reinforced, plastic polymer, composite of the present invention can be prepared by dispersing a reinforcing agent coated with a carboxy terminated butadiene rubber in an epoxy resin at con-
30 ditions sufficient to react the carboxyl groups of the rubber with the residual epoxide groups of the epoxy resin. These conditions are generally achieved in a conventional melt blending operation.

Alternatively, although the elastomer and polymer matrix are not chemically reactive, it is possible that the elastomer, without modification, is sufficiently compatible with the polymer matrix for the purposes of this invention. For example, sufficient compatibility can be obtained by grafting the reinforcing agent with an elastomeric material merely having chemically similar groups or substantially similar solubility parameters to the polymer matrix phase. Specifically, the rubber can be prepared from the same monomer or containing the same groups, either as a block or in random order, as contained by the monomers used in preparing the polymer matrix or the resulting polymer matrix.

For example, an EPDM rubber is sufficiently compatible with a polyolefin plastic material such that a reinforced, plastic polymer, composite of the present invention can be prepared by initially grafting the reinforcing agent with an EPDM rubber and subsequently dispersing the EPDM coated reinforcing agent through a polyolefin, e.g., polyethylene. In view of this compatibility, EPDM is a preferred rubber for preparing the elastomeric coating on the reinforcing agent of a reinforced, plastic polymer, composite of the present invention derived from a polyolefin.

Similarly, a styrenic polymer can be rendered compatible with an acrylic type rubber by copolymerizing a small amount of an alkyl ester of an unsaturated carboxylic acid (i.e., an acrylate) such as methyl methacrylate with the monovinylidene aromatic compound.

The reinforced, plastic polymer, composite of the present invention can subsequently be prepared by incorporating the acrylic rubber coated, reinforcing agent within the acrylate modified polystyrene.

5 Alternatively, the rubber can be modified, without being made chemically reactive in respect to the polymer forming the continuous matrix phase, to render the elastomeric coating sufficiently compatible with the polymer matrix phase. Specifically, one or
10 more block(s) of a polymer which is compatible with the polymer matrix phase can be grafted or otherwise bonded to the rubber to make the elastomeric coating sufficiently compatible with the polymer matrix phase. As used in this sense, the term "compatibility" means
15 that the polymer which constitutes the blocks grafted or otherwise bonded to the rubber, although not necessarily in thermodynamic equilibrium, would behave mechanically as if it were in thermodynamic equilibrium.

20 For example, in preparing a reinforced, plastic polymer, composite of the present invention having a matrix phase of a styrenic polymer, the reinforcing agent can be coated with a block copolymer of an alkadiene and a comonomer which is suitable
25 compatible with the styrenic polymer and thus coated, reinforcing agent subsequently blended with the styrenic polymer resin to form the reinforced, plastic polymer, composite. In this case, it is not necessary that the rubber chemically react with the polymer of the
30 matrix due to the compatibility imparted to the composite by the polystyrene blocks grafted or otherwise

bonded to the rubber which forms the elastomeric coating. For example, the reinforcing agent can be coated with a block copolymer having one or more block(s) of a polymerized 1,3-conjugated diene such as polybutadiene and at least one block of polystyrene grafted or otherwise bonded thereto. The polystyrene block or graft provides the elastomeric coating with the desired compatibility to form a reinforced, plastic polymer, composite of the present invention. Preferably, in preparing a reinforced, plastic polymer, composite of a reinforced styrenic polymer matrix, the block or graft copolymers employed comprise at least 40, more preferably from 65 to 85, weight percent 1,3-butadiene and up to 60, more preferably from 15 to 35, weight percent of a monovinylidene aromatic compound, preferably styrene.

Similarly, when the polymer matrix comprises a copolymer of a monovinylidene aromatic compound such as styrene and a comonomer such as unsaturated nitrile, e.g., acrylonitrile, the reinforcing agent is advantageously coated with graft copolymer having one or more block(s) of a polyalkadiene, preferably polybutadiene, grafted with one or more block(s) of a copolymer of a monovinylidene aromatic compound and an unsaturated nitrile grafted or otherwise bonded thereto.

Similarly, rubber of an alkadiene homopolymer is not sufficiently compatible with a polyphenylene oxide for the purposes of forming a reinforced, plastic polymer, composite of the present invention. Therefore, it is generally advantageous to employ a block copolymer

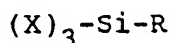
having one or more block(s) of a polyalkadiene, preferably polybutadiene, and at least one block of a monovinylidene aromatic compound, preferably polystyrene, grafted or otherwise bonded to the polyalkadiene block
5 to coat the reinforcing agent. The resulting reinforcing agent coated with the block copolymer of styrene and butadiene can then be dispersed throughout the polyphenyloxide matrix invention.

Alternatively, if the elastomeric coating on
10 the reinforcing agent is not compatible with the polymer matrix phase, rather than chemically modifying the elastomeric coating and/or the polymer matrix phase, a compatibilizing agent can be employed to provide the desired compatibility between the elastomeric coating
15 and the polymer matrix. In general, by properly selecting the rubber or rubber containing copolymer to coat the reinforcing agent, it is not generally necessary to employ an additional compatibilizing agent when incorporating the elastomeric coated reinforcing agent in
20 the continuous matrix of the plastic polymer. However, if required or desired, the compatibilizing agents which are most advantageously employed are depended on the specific plastic polymer and elastomeric coating employed and materials which can be employed as com-
25 patibilizing agents will be readily apparent to the skilled artisan or can be determined by the skilled artisan using simple experimental techniques.

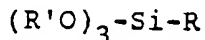
For optimum performance of the elastomeric coating as an interlayer, the elastomeric coating is
30 advantageously coupled to the reinforcing agent. Preferably, such coupling is evidenced by any adhesive

or cohesive failure occurring in the rubber phase as compared to the rubber/glass interface. This coupling is preferably obtained by chemically bonding the reinforcing agent to the continuous polymer matrix. To
5 promote this chemical bonding (i.e., chemical grafting of the elastomer to the reinforcing agent), the rubber can contain silane groups such as the rubbers described in U.S. Patent No. 3,900,629. Alternatively, the
10 reinforcing agent is advantageously coated with a coupling agent which acts to couple the mineral reinforcing agent with the elastomer. Coupling agents suitably employed herein are any material which adhere to the reinforcing agent and which contain a group
15 reactive with the elastomer. In general, the desired chemical bonding results from the reaction of ethylenic unsaturation in both the elastomer and the coupling agent.

In the coating of silicon containing materials (i.e., mica, glass or silicon), silanes which contain
20 a group reactive with the rubber of the elastomeric coating, thereby bonding the rubber to the reinforcing agent, can be employed. In general, since the elastomeric coating is often prepared using a alkadiene rubber, the reactive silanes most commonly employed in the practice
25 of the present invention are those silanes having an ethylenic unsaturation capable of reacting with the residual ethylenic unsaturation of the alkadiene. Hereinafter, these silanes shall be referred to as "vinyl silanes". Representative vinyl silanes include
30 trihalovinyl silanes as represented by the general structural:



wherein X is a halogen, preferably chlorine and R is a hydrocarbon or an inertly substituted hydrocarbon group containing ethylenic unsaturation such as $H_2C=CH(CH_2)$ (e.g., vinyl trichlorosilane); the
5 vinyl alkoxysilanes as represented by the general structural formula:



where in R is an hereinbefore defined and R' is an alkyl, preferably an alkyl having from 1 to 4 carbon
10 atoms (e.g., vinyl triethoxy silane); the vinylester silanes such as a vinyltriacetoxysilane; the acrylic silanes such as methacryloxyalkyl silane and cationic vinylbenzene trimethoxy silane. Of the reactive silanes,
15 vinyl triethoxy silane and cationic vinylbenzyl trimethoxy silane are preferred.

A representative vinyl coupling agent useful in sizing or coating titanate fibers is isopropyl triisostearyl titanate. Alternatively, the grafting
20 of the rubber to the graphite fiber can be promoted forming chemical groups on the reinforcing agent which groups are reactive with the elastomer such as by the oxidative treatment of the fibers such as by wet, dry or electrochemical oxidation.

Alternatively, groups other than ethylenic
25 unsaturation can be employed to bond the elastomeric coating to the mineral fibers. For example, the elastomeric coating can be prepared from a rubbery copolymer having oxyacyl (acrylate) or carboxy groups

coreactive therewith. Specifically, when the elastomer contains carboxyl groups, the coupling agent can contain hydroxyl or amino groups.

In the preparation of the reinforced, plastic polymer, composite, the reinforcing agent is initially coated with the coupling agent, if employed, and the reinforcing agent is initially coated with the coupling agent, if employed, and the reinforcing agent and elastomer are subsequently contacted at conditions sufficient to coat the reinforcing agent and bond the elastomeric coating to the reinforcing agent or coupling agent.

In many cases, glass fibers as well as other reinforcing agents can be purchased having the desired coupling agent previously applied thereto. Alternatively, the reinforcing agent, which may or may not be previously coated with another coupling agent, is coated with the reactive coupling agent by simply dipping or otherwise suspending the resulting reinforcing agent coated with the coupling agent.

If purchased untreated or unsized, the amounts of the coupling agent employed in sizing the reinforcing agent are dependent on a variety of factors including the particular reinforcing agent, coupling agent and elastomer employed. In general, the coupling agent is advantageously employed in an amount from 0.01 to 15, preferably from 0.1 to 5, weight percent based on the total weight of the reinforcing agent. Within said compositional limitation, in the preparation of a glass fiber reinforcement coated with an elastomer of a 1,3-butadiene, the vinyl silane is preferably

employed in an amount from 0.2 to 2, more preferably from 0.5 to 1.5, weight percent based on the total weight of the glass reinforcing agent.

Once the coupling agent, if any, has been
5 applied to the reinforcing agent, any of a variety of techniques can be employed to apply the elastomer to the reinforcing agent. In a preferred method for coating glass reinforcement with the elastomer, the glass,
10 which is dispersed in an organic or aqueous liquid, preferably an organic liquid, to separate the individual monofilaments and the thus separated monofilaments are subsequently contacted with the elastomer at conditions sufficient to react the elastomer with the reactive
15 coupling agent, thereby grafting the elastomer to the glass monofilaments. In a preferred method using these techniques, the elastomer is applied from solution in an organic liquid.

The organic liquid reaction diluents suitably employed in this coating operation are those organic
20 liquids which are capable of dissolving the rubber and which are sufficiently inert to the rubber, reinforcing agent and coupling agent, if employed, to allow the grafting of the rubber to the reinforcing agent. The specific organic liquids most advantageously
25 employed are dependent on a variety of factors, particularly the rubber employed.

Representative examples of organic liquid reaction diluents useful herein in combination with a rubber of an alkadiene include the aromatic hydro-
30 carbons such as ethylbenzene, toluene and styrene and

the chlorinated hydrocarbons such as methylene chloride and dichloroethane. Alternatively, if an EPDM rubber is employed in preparing the elastomeric coating, the organic liquid reaction diluent is advantageously an aromatic hydrocarbon such as toluene, benzene, tetrahydronaphthalene or decahydronaphthalene; a long chain alkyl such as iso-octane or a chlorinated aromatic hydrocarbon such as trichlorobenzene.

Although the application of the elastomer as a coating on reinforcing agent can be conducted at sufficiently elevated temperatures and times to cause reaction between the coupling agent (or reinforcing agent if no coupling agent is employed) and the elastomer without external catalyst or initiator, a catalyst or initiator is often advantageously used in the coating operation. As an example, when coupling the elastomeric coating to the reinforcing agent by reaction of ethylenic unsaturation in both the coating and the polymer matrix or using other groups which react by free-radical means, the reaction is preferably conducted in the presence of a free-radical initiator, thereby reducing the times and/or temperatures required for this coupling operation.

The means for free-radical initiation suitably employed herein include UV radiation and those materials capable of generating free-radicals at the grafting conditions. Initiators which have such ability are readily determined by those skilled in the art. Representative of such initiators are oxygen and the peroxide initiators such as the peresters,

e.g., tertiarybutyl peroxy benzoate and tertiary butylacetate, dibenzoylperoxide, dilaurylperoxide, 1,1-bistertiary butyl peroxy cyclohexane, 1,1-bis-(tertiarybutylperoxy)-3,3,5-tri-methylcyclohexane, 5 dicumylperoxide; and the azo compounds such as azobisisobutyronitrile. Preferred initiators include dibenzoylperoxide, tertiarybutylperoxybenzoate 1,1-bis-(tertiarybutylperoxy)-3,3,5-tri-methylcyclohexane.

10 The concentration at which the free-radical initiator is employed is dependent on a variety of factors including the specific initiator, coupling agent, if any, and elastomer employed and the times and temperatures used in the operation. In general, the free-radical initiator is employed in an amount 15 from 0.01 to 10 weight percent based on the total weight of the elastomer. Preferably, the free-radical initiator is employed in an amount from 10 to 10,000 more preferably in an amount from 100 to 1000, parts by weight, per million weight parts of 20 the elastomer.

Using the described initiators and ethylenic unsaturation to couple the elastomeric coating with the reinforcing agent, the temperatures at which the coating operation is conducted will vary depending 25 on the specific elastomer and reactive coupling agent employed. In general, temperatures from 30°C to 150°C will be employed. Preferably, the coating of the elastomer on the reinforcing agent is conducted at temperatures from 50 to 130°C, more preferably from 70 to 120°C.

Other catalysts and/or initiators which can be employed are dependent on the particular coupling reaction and are readily apparent to those skilled in the art.

5 Following the coating operation, the thus coated reinforcing agent is subsequently dispersed throughout the plastic polymer matrix. Preferably, the reinforcing agent is uniformly dispersed throughout the polymer matrix. This can be conducted using
10 any of a number of different techniques. The preferred methods for dispersing the elastomer coated reinforcing agents are dependent on the specific elastomer coating reinforcing agents and the polymer plastic materials employed. For example, it is possible to merely blend
15 the reinforcing material coated with the elastomer and the plastic polymer using conventional blending techniques. In general, of the blending techniques, melt blending is preferred. By the term "melt blending" it is meant the blending of the plastic polymer
20 in a molten or liquid state with the elastomer coated, reinforcing agent.

 Alternatively, the composite can be prepared by initially dispersing the elastomer coated, reinforcing material in an organic liquid, preferably an
25 organic liquid which does not dissolve the elastomeric coating. Subsequently, the plastic polymer is added and dissolved or melted in the dispersion of the organic liquid and reinforcing agent. The organic liquid diluent is then removed to form the reinforced, plastic polymer,
30 composite. If the elastomeric coated, reinforcing agent is prepared in an organic liquid, the polymer

can often be directly added to the resulting dispersion without subsequent separation of the coated reinforcing agent from the organic liquid.

In yet another embodiment, the reinforced,
5 plastic polymer, composite can be prepared by dispersing the elastomer coated, reinforcing agent in a solution or dispersion of the monomer(s) which when polymerized will form the plastic polymer matrix, and thereafter, polymerizing said monomers.

10 For example, a reinforced, plastic polymer, composite comprising a styrenic polymer resin matrix can be prepared by dispersing the elastomer coated, reinforcing agent throughout the monomer(s) which, when polymerized, will form the desired polymer
15 matrix. This embodiment is particularly useful in the preparation of a composite having a styrenic polymer matrix. Thereafter, the resulting dispersion, i.e., the monomer(s) having the elastomeric coated, reinforcing agent dispersed therethrough,
20 is subjected to conditions sufficient to polymerize the polymerizable monomer(s) and form the desired reinforced, plastic polymer, composite.

In this embodiment of the present invention, although the polymer can be polymerized using emulsion
25 polymerization techniques, conventional mass or mass/-suspension polymerization techniques are generally most advantageously employed in polymerizing the monomer(s) to prepare the composites. In such case, any rubber present in the original polymerization
30 mixture which is not bonded to the reinforcing agent

will become dispersed as discrete particles throughout the resulting plastic polymer matrix. Although the mass polymerization can be conducted using any of a variety of batch or continuous polymerization techniques, it is advantageously conducted using continuous polymerization techniques in one or more substantially linear stratified flow or so-called plug flow reactors such as described in U.S. Patent No. 2,727,884, which may or may not comprise recirculation of a portion of the partially polymerized product.

Using these techniques, the mass polymerization is advantageously conducted in the presence of an organic liquid reaction diluent such as an aromatic hydrocarbon or inertly substituted aromatic hydrocarbon (e.g., benzene or toluene) and in the presence of a free-radical initiator such as a peroxide initiator (e.g., dibenzoyl peroxide or 1,1-bis-(tertiarybutylperoxy cyclohexane). In general, the initiator will be employed in an amount from 100 to 50,000 weight parts per million weight parts of the monomer employed. The organic liquid reaction diluent is conventionally employed to control the viscosity of the polymerization mixture and will generally be employed in an amount from 2 to 20 weight percent based on the total weight of the monomers, the elastomeric coated reinforcing agent, and, if employed, the rubber and organic liquid reaction diluent. The mass polymerization mixture can further contain other adducts such as a plasticizer or lubricant (e.g., mineral oil), an antioxidant (e.g., an alkylated phenol

such as di-tert-butyl-p-cresol), a polymerization aid (e.g., a chain transfer agent such as alkyl mercaptan) or a mold release agent (e.g., zinc stearate).

Temperatures at which polymerization is
5 conducted are dependent on the specific components employed but will generally vary from 75° to 225°C, preferably 90° to 190°C. In the preparation of the reinforced, plastic polymer, composites, polymeriza-
10 tion is continued to the desired degree of completion and the resulting polymerization product is then treated to remove any unreactive monomer such as by flashing of the monomer and other volatiles at an elevated temperature under vacuum.

The following Examples are set forth to
15 illustrate the advantages of the present invention and should not be construed to limit its scope. In the Examples all parts and percentages are by weight unless otherwise indicated.

Example 1

20 An elastomer coated glass fiber is prepared by initially dissolving, in 90 parts of ethylbenzene, 4.5 parts of a rubber of polymerized 1,3-butadiene having 5.5 parts of a copolymer derived from 75 percent styrene and 25 percent acrylonitrile grafted as blocks
25 to the rubber molecules. Subsequently, 20 parts of glass fibers (i.e., a bundle of individual microfibers or monofilaments, each microfiber having a diameter of from 10 to 13 microns and a length of from 45 to 60 millimeter (mm), sold under the tradename of
30 414X7 by Owens Corning Fiberglas, are dispersed in

the ethylbenzene/rubber solution to cause the individual monofilaments of the glass fiber to be dispersed throughout the solution. After dispersing the monofilaments in the ethylbenzene/rubber solution, 0.5
5 parts of an antioxidant sold under the tradename of Irganox 1076 by Ciba Geigy was introduced into the solution. The ethylbenzene/rubber solution having the monofilaments dispersed therein was subsequently heated to 115°C. When the resulting dispersion obtained
10 this temperature, 200 parts per million, based on the parts of the copolymer employed to coat the reinforcing agent, of 1,1 di-tert-butyl peroxy cyclohexane was added. The resulting dispersion was maintained at 115°C
15 for 1 hour, with continuous stirring. At the end of this time, essentially all the dissolved rubber was found to have been grafted to the glass fiber. The resulting elastomer coated glass fiber comprised 30 percent grafted rubber based on the total weight of the glass fiber, rubber and grafted styrene/acrylonitrile copolymer.
20

A reinforced, plastic polymer, composite of the present invention was prepared by melt blending the resulting rubber coated, glass fibers with a copolymer of styrene and acrylonitrile. Specifically, a copolymer
25 consisting of 75 percent polymerized styrene and 25 percent polymerized acrylonitrile was dissolved in methylene chloride. The resulting solution was poured into the ethylbenzene solution containing the dispersed elastomer coated glass fibers. The resulting
30 dispersion comprising ethylbenzene, rubber coated glass fibers, methylene chloride and a copolymer of styrene and acrylonitrile was heated to 115°C, with

continuous agitation, for 45 minutes. At this time, the resulting product is placed in a vacuum oven (mmHg) at 170°C to remove the ethylbenzene and methylene chloride. The resulting product is a reinforced,
5 plastic polymer, composite comprising a styrenic polymer matrix of a copolymer of polymerized styrene and acrylonitrile having rubber coated, glass fibers dispersed thereto.

Example 2

10 The procedure of Example 1 is repeated except that 30 parts of glass fibers identical to those employed in Example 1 were coated with 4.5 parts of a 1,3-butadiene rubber grafted with 5.5 parts of a copolymer of styrene and acrylonitrile.

15 A glass reinforced copolymer of styrene and acrylonitrile was prepared by melt blending 60 parts of a copolymer of styrene and acrylonitrile identical to that employed in Example 1 with 40 parts of the rubber coated, glass fibers.

20 Comparative Example A

Seventy parts of a copolymer of styrene and acrylonitrile was melt blended with 20 parts of glass fibers identical to those employed in Example 1 except not coated with an elastomer layer and 10 parts of
25 a rubbery copolymer. The rubber has the same composition as the rubber employed in Example 1 and was prepared at a weight average particle size of 0.2 micron using emulsion polymerization techniques. Essentially none of the rubber became bonded to the glass fiber during
30 the melt blending operation. The resulting melt blended product consisted of a styrenic polymer matrix having

the glass fibers and discrete particles of the rubber dispersed as 0.2 micron particles therethrough.

Comparative Example B

- 5 A copolymer of styrene and acrylonitrile reinforced with glass fibers was prepared by melt blending 80 parts of a copolymer of styrene and acrylonitrile identical to that employed in Example 1 with 20 parts of glass fibers (not coated) identical to those employed in Comparative Example A.

10 Comparative Example C

- A rubber-reinforced copolymer of styrene and acrylonitrile is prepared by melt blending 90 parts of a copolymer of styrene and acrylonitrile identical to that employed in Example 1 with 10 parts
15 of a rubber identical to that employed in Comparative Example A. The rubber is dispersed throughout the copolymer of styrene and acrylonitrile as discrete rubber particle having a volume average particle size of 0.2 micron.

20 Comparative Example D

A copolymer of styrene and acrylonitrile was prepared, which is identical to the copolymer employed in preparing the composite of Example 1. It is not further reinforced with glass fibers or rubber.

- 25 The high temperature properties, as indicated by the Vicat softening point, the tensile properties and the impact strengths of the resulting products were measured. The results of these measurements are set forth in Table I.

TABLE I

		<u>Example</u>	<u>Example</u>	<u>Comparative Example</u>			
		<u>1</u>	<u>2</u>	<u>A*</u>	<u>B*</u>	<u>C*</u>	<u>D*</u>
	<u>Polymer</u>						
5	<u>Composite</u>						
	<u>Wgt % (1)</u>						
	<u>SAN</u>	70	60	70	80	90	100
	<u>Glass</u>						
	<u>Fiber</u>	20	30	20	20	-	-
10	<u>Elastomer</u>	10	10	10	-	10	-
	(% PBD)	(4.5)	(4.5)	(4.5)	-	(4.5)	-
	<u>High Temperature Properties (2)</u>						
	Viscat, °C	128	138	119	119	108	108
15	HDT, °C	102	107	102	102	80	85
	<u>Tensile Properties (3)</u>						
	Tensile Yield, N/mm ²	75	88	90	102	50	67
	Elongation, %	5	5	5	5	50	5
20	Flexural Modulus, N/mm ²	5100	5450	6500	6800	2750	3000
	<u>Impact Strength (4)</u>						
	Izod, J/m (20°C)	261	400	64	59	44	16

*Not an example of the present invention

1. The composition of the polymer composite is set forth in weight percent based on the total weight of the composite. Each component of the composite is set forth in abbreviated form wherein:
 - 5 SAN = copolymer comprising 84-75 parts of polymerized styrene and 16-25 parts of polymerized acrylonitrile

Glass fiber = chopped glass fibers sold as 414X7 by Owens-Corning
 - 10 Elastomer = block copolymer comprising 45 parts of block of polymerized 1,3-butadiene and 55 parts of a copolymer block of a random copolymer derived from 75 percent styrene and 25 percent acrylonitrile.
- 15 2. The high temperature properties of the composite indicated by the Vicat and the Heat Distortion Temperature. The Vicat as measured using the test method described by ASTM D-1525. The heat distortion temperature was measured by using DIN
20 test method 53461.
- 25 3. Tensile properties were measured using the test method of ASTM-D-638 on samples which were injection molded at a melt temperature of 250°C. The tensile yield and flexural modulus are expressed in Newtons per square millimeter (mm²) and elongation being the elongation at break expressed as a percentage of the original length.
- 30 4. Izod impact strength is the notched Izod impact expressed in Joules/meter (J/m) measured using the test method described by ASTM D-256 on test specimens which were injection molded as described in footnote 3.

As evidenced by the data set forth in Table I, the composites of the present invention exhibit unexpectedly superior high temperature properties, tensile properties and impact strengths as compared to the reinforced, styrenic polymer resin composites which are not reinforced with glass fibers coated with an elastomer.

Example 3

Glass fibers coated with an EPDM rubber were prepared by dissolving an EPDM rubber in sufficient amounts of trichlorobenzene to form a 7 percent solution. To aid in the dissolution of the rubber, the trichlorobenzene was heated to 140°C. Following preparation, the resulting rubber solution is cooled by the addition of sufficient amounts of trichlorobenzene to form a 5 percent solution of the rubber in the trichlorobenzene. In addition, 0.5 parts of an antioxidant sold under the tradename of Irganox 1076 was added to the resulting solution.

At this time, 20 parts sized fibers of chopped glass fibers sold as 415 YZ by Owens-Corning were added with additional amounts of trichlorobenzene to aid in dispersing the glass fibers as individual microfilaments throughout the solution. Once the monofilaments are sufficiently dispersed throughout the rubber solution, the temperature of the dispersion was increased to 115°C. At this time, 500 parts per million, based on the parts of the rubber (i.e., the EPDM) applied to the glass reinforcing agent, of a free-radical initiator sold as Triganox 22E50 by Interlox was introduced into the dispersion. This dispersion was maintained for a one hour period, with continuous agitation, at a temperature of

115°C, thereby grafting the EPDM rubber to the glass fibers. Without cooling the resulting dispersion, 75 parts of high density polyethylene is added to the dispersion of the glass fibers now coated with the EPDM rubber. The temperature of the dispersion was then increased to 125°C and the material was stirred until the high density polyethylene was molten and dissolved in the trichlorobenzene. Agitation of the dispersion was continued for an additional 30 minutes. At this time, the resulting product was placed in a vacuum over (5 mmHg) for 90 minutes at 180°C.

The resulting product comprised 75 parts of the high density polyethylene, 20 parts of the glass fibers and 5 parts of the EPDM rubber grafted to the glass fibers.

Example 4

A reinforced polymer composite of high density polyethylene and glass fibers coated with an EPDM rubber was prepared using identical techniques to that of Example 3 except that 30 parts of the glass fibers are employed in preparing the elastomer coated glass fiber and only 65 parts of the high density polyethylene is subsequently added to the dispersion containing the elastomeric coated, glass fibers. The resulting product comprised 65 percent of the high density polyethylene is subsequently added to the dispersion containing the elastomeric coated, glass fibers. The resulting product comprised 65 percent of the high density polyethylene, 30 percent of the glass fibers and 5 percent of the EPDM rubber grafted to the glass monofilament.

Comparative Example E

A glass fiber reinforced, high density polyethylene, composite is prepared by melt blending 75 parts of a high density polyethylene identical to the high density polyethylene employed in preparing the composite of Example 3 and 20 parts of glass fibers identical to those employed in Example 3 except not coated with an elastomeric coating and 5 parts of an EPDM rubber. The EPDM rubber has the same composition of the rubber of Example 3 but does not serve as an interlayer between the reinforcing agent and the plastic polymer matrix.

Comparative Example F

A high density polyethylene reinforced with glass fibers was prepared by melt blending 70 parts of high density polyethylene identical to that employed in Example 3 with 30 parts of glass fibers identical to those employed in Comparative Example E.

Comparative Example C

A high density polyethylene identical to that of Example 3 was prepared. It was not further reinforced with glass fibers or an EPDM rubber.

The flexural modulus, Izod impact strength and heat distortion temperatures of the resulting products were measured. The results of these measurements are indicated in Table II.

TABLE II

	<u>Polymer</u>	<u>Example</u>	<u>Example</u>	<u>Comparative Example</u>		
		<u>3</u>	<u>4</u>	<u>E*</u>	<u>F*</u>	<u>G*</u>
5	<u>Composite</u>					
	<u>Wgt % (1)</u>					
	<u>HDPE</u>	75	65	70	80	100
	<u>Glass Fiber</u>	20	30	30	20	-
10	<u>EPDM Elastomer</u>	5	5	5	-	-
	<u>High Temperature Properties (2)</u>					
	<u>Viscat, °C</u>	132	132	128	138	125
15	<u>HDT, °C</u>	124	127	121	115	44
	<u>Tensile Properties (3)</u>					
	<u>Tensile Yield, N/mm²</u>	38	45	45	45	28
	<u>Elongation, %</u>	6	6	6	8	100
20	<u>Flexural Modulus, N/mm²</u>	2050	3400	2500	2600	950
	<u>Impact Strength (4)</u>					
	<u>Izod, J/m (20°C)</u>	295	336	170	102	180

*Not an example of the present invention

- 5 (1) Same as footnote (1) in Table I except:
HDPE = high density polyethylene having a density
of 0.957 g/cc and a melt index of 1.3 g/10 minutes.
EPDM = an elastomeric copolymer of 35 percent ethylene,
56 percent propylene and 9 percent 1,3-butadiene.
- (2) Same as footnote (2) in Table I
(3) Same as footnote (3) in Table I
(3) Same as footnote (4) in Table I

Again, the composites of the present invention exhibit an unexpected balance of properties.

Example 6

- To sufficient amounts of ethylbenzene to
- 5 prepare a 10 percent rubber solution is added 4.3 parts of a rubber of 1,3-butadiene grafted with 7 parts of a random copolymer of styrene and methyl methacrylate sold under the tradename of Paraloid BTA III FF1 by Rohm and Haas. To the resulting solu-
- 10 tion was added 0.5 parts of an antioxidant sold as Irganox 1076 by Ciba Geigy. Subsequently, 20 parts of glass fibers sold as 414X7 by Owens Corning were dispersed in the resulting rubber solution. After the complete dispersion of the fibers as monofilaments
- 15 throughout the rubber solution, the resulting dispersion was heated to 115°C. When the dispersion reached this temperature, 200 parts per million, based on the total parts of the copolymer applied to the glass fiber (i.e., the total amount of grafted rubber, inclu-
- 20 ding the polybutadiene and the grafted copolymer blocks) of a peroxide initiator were added. The dispersion was maintained at 115°C for one hour, with continuous agitation to allow the copolymer rubber to graft to the glass fibers.
- 25 Subsequently, a solution comprising 120 parts of a polycarbonate sold as XP-73010 by the Dow Chemical Company in 500 parts methylene chloride was added to the resulting dispersion. The mixture was maintained at 115°C, with agitation, for an additional 30 minutes.
- 30 At this time, the resulting reinforced, plastic polymer, composite was placed in a vacuum oven (5 mm Hg) for 2 hours fo 180°C to remove the ethylbenzene and methylene chloride

solvents. The resulting reinforced, polycarbonate composite exhibited a Vicat softening point of 164°C, a heat distortion temperature of 140°C and an Izod impact strength of 353 Joules/meter. The tensile yield of
5 the composite was 75 Newtons/square millimeter; the elongation was 5 percent; and the flexural modulus was 400 Newtons/square millimeter. All properties were measured by the testing techniques set forth in the footnotes to Table I.

10 Example 7 and Comparative Examples H-K

An elastomer coated glass fiber was prepared by initially dissolving, in 90 parts of ethylbenzene, 10 parts a block copolymer (Bayer's Buna B 30 percent styrene/70 percent 1,3-butadiene).

15 Subsequently, 20 parts of chopped strand glass fiber, sold under the trade name of 429 under the trade name of 429 ZZ by Owens Corning, were dispersed in the ethylbenzene/rubber solution to cause the individual monofilaments of the glass fiber to
20 be dispersed throughout the solution. After dispersing the monofilament in the ethylbenzene/rubber solution, 0.5 parts of Irganox 1076 was introduced into the solution. The ethylbenzene/rubber solution having the monofilaments dispersed therein was subsequently heated to 115°C. When the resulting disper-
25 sion reached this temperature, 200 ppm of 1,1-ditertiarybutylperoxy cyclohexane was added. The resulting dispersion was maintained at 115°C for 1 hour, with continuous stirring. At the end of this time, most
30 of the dissolved rubber was found to have been grafted to the silane phase of the glass fiber.

Transmission Electron Micrograph technique was used to visualize the grafted polybutadiene phase. Samples were treated with a diluted solution of hydrofluoric acid to dissolve the glass fiber; with polybutadiene phase was stained with osmium tetroxide. It was then clearly seen that the glass fiber was very well protected by a thin rubber layer ranging from 0.5 to 1.5 micron, while the polystyrene block of the copolymer was completely miscible with the polystyrene matrix phase.

A reinforced styrenic polymer composite was prepared by solvent blending of the block copolymer rubber coated glass fiber with polystyrene (Dow Chemical's STYRON E 680) dissolved in methylene chloride, with continuous stirring for 45 minutes. At this time, the resulting product was placed in a vacuum oven at 180°C to remove the rest of the solvent. Compression molded specimens of the resulting product were tested in comparison with samples prepared by the melt blending of the silane coated glass fiber and polystyrene matrix.

From Table III, it appears that several physical properties of the composite prepared by the grafting technique are improved (i.e. impact strength, flexural modulus and heat distortion temperature, etc.,....) in comparison with the base polystyrene product. For comparison purposes, physical properties of polystyrene and of melt blended samples of styrene-butadiene block copolymer in polystyrene are also presented in Table III.

TABLE III: Physical properties of fiber reinforced Styrenic polymer

		<u>Example</u> <u>7</u>	<u>Comparative Examples</u>			
			<u>H*</u>	<u>I*</u>	<u>J*</u>	<u>K*</u>
<u>Polymer composite wgt % (1)</u>						
5	PS	70	70	90	80	100
	Glass fiber	20	20	-	20	-
	Elastomer	10	10	10	-	-
	(% PDB)	(7)	(7)	(7)		
<u>High temperature</u> <u>Properties (2)</u>						
10	Vicat, °C	116	111	104	112	106
	HDT, °C	98	98	78	101	80
<u>Tensile propertie (3)</u>						
	Tensil yield, N/mm ²	55	60	25	70	45
15	Elongation, %	5	5	40	5	5
	Flexural modulus, N/mm ²	4500	5200	2500	5800	3500
<u>Impact strength (4)</u>						
	Izod, J/m (20°C)	192	66	65	54	15
20	1. The composition of the polymer composite is set forth in weight percent based on the total weight of the composite. Each component of the composite is set forth in abbreviated form wherein:					
	PS	: Dow Chemical's STYRON E 680				
	Glass fiber:	Chopped glass fibers sold as 429 ZZ by Owens-Corning.				
25	Elastomer	: Styrene-butadiene block copolymer sold as Buna B-6245 by Bayer.				

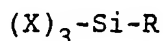
2. The high temperature properties of the composite are indicated by the Vicat and the heat distortion temperature. The Vicat as measured using the test method described by ASTM D-1525/B. The heat distortion temperature was measured by using DIN test method 53461.
5
3. Tensile properties were measured using the test method of ASTM-D-638 on samples which were injection molded at a melt temperature of 250°C.
4. Izod impact strength is the notched izod impact expressed in Joules/meter (J/m) measured using the test method described by ASTM-D-256 on test specimens which were injection molded as described in footnote 3.
10

1. A reinforced polymer composite of the type including (a) a plastic polymer matrix; (b) a reinforcing agent; and (c) an interlayer between the polymer and the reinforcing agent; characterized in that the interlayer (1) is elastomeric; and (2) is directly or indirectly bonded to the reinforcing agent.
2. The composite of Claim 1 wherein the elastomeric material is adhered or coupled to the reinforcing agent by a coupling agent having functional groups reactive with the reinforcing agent and the elastomeric material; (2) the plastic polymer matrix is a thermoplastic plastic; and (3) the interlayer has a thickness in the range from 500 to 50,000 Å.
3. The composite of Claim 2 wherein the reinforcing agent is mica or glass.
4. The composite of Claim 3 wherein the reinforcing agent is glass monofilament having a length, in the composite, from 0.1 to 50 millimeters and a diameter from 1 to 100 microns; and wherein the interlayer is present in an amount of at least 5 percent based on the weight of reinforcing agent.

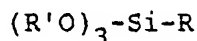
5. The composite of Claim 4 wherein the coupling agent is a silane having a group reactive with the rubber which forms the elastomeric coating.

6. The composite of Claim 5 wherein the rubber employed in preparing the elastomeric coating is derived, at least partially, from an alkadiene rubber and the coupling agent is a vinyl silane.

7. The composite of Claim 5 wherein the trihalovinyl silanes as represented by the general structural formula:



wherein X is a halogen, preferably chlorine and R is a hydrocarbon or an inertly substituted hydrocarbon group containing ethylenic unsaturation; the vinyl alkoxy silanes as represented by the general structural formula:



wherein R is as hereinbefore defined and R' is an alkyl, preferably an alkyl having from 1 to 4 carbon atoms; the vinylester silanes; the acrylic silanes and cationic vinylbenzene trimethoxy silane.

8. The composite of Claim 7 wherein the vinyl silane coupling agent is vinyl triethoxy silane or cationic vinyl benzyl trimethoxy silane.

9. The composite of Claim 7 wherein the rubber employed in preparing the elastomeric coating is a homopolymer or copolymer of a 1,3-conjugated diene.

10. The composite of Claim 7 wherein the rubber employed in preparing the elastomeric coating exhibits a single order glass transition temperature which is not higher than 0°C.

5 11. The composite of Claim 9 wherein the rubber employed in preparing the elastomeric coating is a homopolymer or copolymer of butadiene.

12. The composite of Claim 4 wherein the plastic polymer matrix is a thermosettable plastic.

10 13. The composite of Claim 12 wherein the plastic polymer matrix is a vinyl ester resin, an epoxy resin, a polyester resin, an amino resin, a silicon resin or a phenolic resin.

15 14. The composite of Claim 1 wherein the interlayer has a thickness in the range from 2,500 to 20,000 Å.

20 15. The composite of Claim 4 wherein the plastic polymer matrix is a resin derived from one or more monovinylidene aromatic compounds and optionally, one or more monomers copolymerizable therewith, an acrylic resin, a polyolefin, a polyurethane or isocyanurate modified polyurethane, a nylon, a polycarbonate, a polyphenylene oxide or a poly(ether ethyl ketone).

25 16. The composite of Claim 15 wherein the plastic polymer matrix is a polymer resin prepared from styrene and, optionally, one or more monomers

copolymerizable therewith, a polycarbonate, a polyphenylene oxide, high density polyethylene, low density polyethylene or linear low density polyethylene.

17. The composite of Claim 16 wherein the plastic polymer matrix is a polyolefin and the elastomeric coating is an EPDM rubber.

18. The composite of Claim 16 wherein the plastic polymer matrix is a polymer resin derived styrene and, optionally, one or more monomers copolymerizable therewith, and the elastomeric coating is derived, at least partially, from an alkadiene.

19. The composite of Claim 16 wherein the plastic polymer matrix is a homopolymer of styrene and the reinforcing agent is coated with a block copolymer having one or more block(s) of polymerized 1,3-conjugated diene and at least one block of polystyrene grafted or otherwise bonded thereto.

20. The composite of Claim 19 wherein the reinforcing agent is coated with a block or graft copolymer comprising from 65 to 85 weight percent 1,3-butadiene and from 15 to 35 weight percent of a monovinylidene aromatic compound.

21. The composite of Claim 18 wherein the plastic polymer matrix is a copolymer of styrene and acrylonitrile and the reinforcing agent is coated with a block copolymer having one or more block(s) of polymerized 1,3-conjugated diene and at least one block derived from styrene and acrylonitrile grafted or otherwise bonded thereto.

22. The composite of Claim 20 or 21 wherein the 1,3-conjugated diene is butadiene and the monovinylidene aromatic compound is styrene.

23. The composite of Claim 16 wherein the plastic polymer matrix is polycarbonate and the elastomeric coating is derived from a block copolymer of a block of a polyalkadiene and at least one block of a random copolymer of a monovinylidene aromatic compound and an unsaturated nitrile compound.

24. The composite of Claim 23 wherein the elastomeric coating is derived from a block copolymer of a block of 1,3-butadiene and at least one block of a random copolymer derived from 80 to 90 weight percent of the monovinylidene aromatic compound and from 10 to 20 weight percent the unsaturated nitrile.

25. The composite of Claim 23 wherein the elastomeric coating is derived from 40 to 90 weight percent of 1,3-butadiene and from 10 to 60 weight percent of a random copolymer of a monovinylidene aromatic compound and an unsaturated nitrile and the monovinylidene aromatic compound is styrene and the unsaturated nitrile compound is acrylonitrile.

26. The composite of Claim 14 wherein the plastic polymer matrix is polyphenylene oxide and the reinforcing agent is coated with a block copolymer having one or more block(s) of a polyalkadiene and at least one block of a monovinylidene aromatic compound grafted or otherwise bonded to the polyalkadiene block.

27. The composite of Claim 26 wherein the alkadiene is 1,3-butadiene and the monovinylidene aromatic compound is styrene.

28. A method for preparing the composite of
5 Claim 1, the method comprising the initial step of coating the reinforcing agent with a layer of an elastomeric material and thereafter incorporating the elastomeric coated, reinforcing agent dispersed throughout the plastic polymer matrix.

10 29. The method of Claim 28 wherein the elastomeric coating is bonded to the reinforcing agent by initially coating the reinforcing agent with a coupling agent and thereafter, the reinforcing agent and elastomer are contacted at conditions suf-
15 ficient to coat the reinforcing agent and bond the elastomeric coating to the reinforcing agent or coupling agent.

30. The method of Claim 29 wherein the reinforcing agent is glass fibers and is sized with the coupling agent by dispersing the glass fiber bundles in
20 an organic or aqueous liquid to separate fibers into individual monofilaments and contacting the thus separated monofilaments with the elastomer.

31. The method of Claim 29 wherein the
25 reinforcing agent coated with the elastomer is dispersed throughout the plastic polymer using melt blending techniques.

32. The method of Claim 29 wherein the method comprising the steps of dispersing the elastomer coated, reinforcing material in an organic liquid; adding and dissolving or melting the plastic
5 polymer in the dispersion of the organic liquid and reinforcing agent and subsequently removing the organic liquid diluent to form the reinforced, plastic polymer, composite.

33. The method of Claim 32 wherein the organic
10 liquid does not dissolve the elastomer.

34. The method of Claim 32 wherein the organic liquid is an aromatic hydrocarbon, a chlorinated hydrocarbon or a long chain alkyl.

35. The method of Claim 28 wherein the
15 method comprises the steps of dispersing the elastomer coated, reinforcing agent throughout the monomer(s) which, when polymerized, will form the polymer matrix, and subjecting the resulting dispersion (i.e., the monomer(s) having the elastomeric coated, reinforcing
20 agent dispersed therethrough) to conditons sufficient to polymerize the polymerizable monomer(s) and form the desired reinforced, plastic polymer, composite.

36. A blend of coated elangated sili-
cious objects characterized in that the coating (1)
25 is elastomeric; (2) is directly or indirectly bonded to the silicious objects; and (3) has a thickness in the range from 1000 to 50,000 Å.

37. The blend of Claim 36 wherein the elongated silicious object is glass having a length from 0.1 to 50 millimeters and a thickness from 1 to 100 microns.

5 38. The blend of Claim 37 wherein the elongated silicious objects (1) are glass monofilaments having random orientation; and (2) the elastomeric coating is in an amount of at least 10 weight percent based on the weight of elongated silicious objects.

10 39. The composite of Claim 1 having an impact resistance greater than the impact resistance of a first control composite, wherein the composite of Claim 1 and the first control composite contain equal total amounts of elastomer, and wherein all
15 the elastomer in the first control sample is dispersed within the polymer matrix.

40. The composite of Claim 1 having an impact resistance greater than the impart resistance of a second control composite, wherein the second
20 control composite contains no elastomer.

41. The composite of Claim having an impact resistance greater than the impact resistance of a third control composite, wherein the third control composite and the composite of Claim 1 contain equal
25 total amounts of elastomer, and wherein there is absence of chemical bonding between the elastomer and the reinforcing agent.

AMENDED CLAIMS

[received by the International Bureau on 11 August 1986 (11.08.86);
original claims 7-11,13,15-27,32-35 and 37-38 deleted;
remaining claims renumbered 1-16 (4 pages)]

1. A reinforced polymer composite of the type including (a) a plastic polymer matrix; (b) a reinforcing agent; and (c) an interlayer between the polymer and the reinforcing agent; characterized in that the interlayer (1) is elastomeric; and (2) is directly or indirectly bonded to the reinforcing agent.
2. The composite of Claim 1 wherein the elastomeric material is adhered or coupled to the reinforcing agent by a coupling agent having functional groups reactive with the reinforcing agent and the elastomeric material; (2) the plastic polymer matrix is a thermoplastic plastic; and (3) the interlayer has a thickness in the range from 500 to 50,000 Å.
3. The composite of Claim 2 wherein the reinforcing agent is mica or glass.
4. The composite of Claim 3 wherein the reinforcing agent is glass monofilament having a length, in the composite, from 0.1 to 50 millimeters and a diameter from 1 to 100 microns; and wherein the interlayer is present in an amount of at least 5 percent based on the weight of reinforcing agent.

5. The composite of Claim 4 wherein the coupling agent is a silane having a group reactive with the rubber which forms the elastomeric coating.

6. The composite of Claim 5 wherein the rubber employed in preparing the elastomeric coating is derived, at least partially, from an alkadiene rubber and the coupling agent is a vinyl silane.

7. The composite of Claim 4 wherein the plastic polymer matrix is a thermosettable plastic.

8. The composite of Claim 1 wherein the interlayer has a thickness in the range from 2,500 to 20,000 Å.

9. A method for preparing the composite of Claim 1, the method comprising the initial step of coating the reinforcing agent with a layer of an elastomeric material and thereafter incorporating the elastomeric coated, reinforcing agent dispersed throughout the plastic polymer matrix.

10. The method of Claim 9 wherein the elastomeric coating is bonded to the reinforcing agent by initially coating the reinforcing agent with a coupling agent and thereafter, the reinforcing agent and elastomer are contacted at conditions sufficient to coat the reinforcing agent and bond the elastomeric coating to the reinforcing agent or coupling agent.

11. The method of Claim 10 wherein the reinforcing agent is glass fibers and is sized with the coupling agent by dispersing the glass fiber bundles in an organic or aqueous liquid to separate fibers into individual monofilaments and contacting the thus separated monofilaments with the elastomer.

12. The method of Claim 10 wherein the reinforcing agent coated with the elastomer is dispersed throughout the plastic polymer using melt blending techniques.

13. A blend of coated elongated silicious objects characterized in that the coating (1) is elastomeric; (2) is directly or indirectly bonded to the silicious objects; and (3) has a thickness in the range from 1000 to 50,000 Å.


14. The composite of Claim 1 having an impact resistance greater than the impact resistance of a first control composite, wherein the composite of Claim 1 and the first control composite contain equal total amounts of elastomer, and wherein all the elastomer in the first control sample is dispersed within the polymer matrix.

15. The composite of Claim 1 having an impact resistance greater than the impact resistance of a second control composite, wherein the second control composite contains no elastomer.

16. The composite of Claim 1 having an impact resistance greater than the impact resistance of a third control composite, wherein the third control composite and the composite of Claim 1 contain equal
- 5 total amounts of elastomer, and wherein there is absence of chemical bonding between the elastomer and the reinforcing agent.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US86/00553

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ²		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 4 B32B 9/04, 17/04, 19/02 US Cl 428/363,429,441; 525/67,71,76,78		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
US	525/67,71,76,78 428/363,429,441,442	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁶		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category ⁸	Citation of Document, ¹⁶ with Indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
A	US,A, 3,655,565 (Minnisota Mining and Manufacturing Co.) 11 APRIL 1972	1-38
X	US,A, 4,318,960 (Owens-Corning Fiberglass Corp.) 9 MARCH 1982	1-3,14,28 29, 31, 36
X	US,A, 4,374,892 (Essex Group Inc.) 22 FEBRUARY 1983	1-3,14,28, 29, 31, 36
P,X	US,A, 4,587,159 (Ow Corning Corp.) 06 MAY 1986	1-3,14,28 29, 31, 36
<div style="display: flex; justify-content: space-between;"> <div style="width: 48%;"> <p>¹⁵ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 48%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"Δ" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ¹	Date of Mailing of this International Search Report ²	
28 MAY 1986	13 JUN 1986	
International Searching Authority ¹	Signature of Authorized Officer ²⁰	
ISA/US	 W. J. VanBalén	

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹⁰

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☒ Claim numbers 39-41 because they relate to subject matter ¹² not required to be searched by this Authority, namely:

Mere presentation of "control" information without reciting entire constitution of each "control".

2. ☒ Claim numbers 41, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ¹³, specifically:

Dependency of the claim missing.

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ¹¹

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.